

Fall 2001 Chem 130A page 1

home-made PROBLEM SET 6 SOLUTIONS

4.11, 4.14, 4.17, 4.21, 4.30

⑩ (a) at constant  $T$ ,  $\mu_i^\circ = \overline{H}_i^\circ - T\overline{S}_i^\circ$

Hence:

$$\begin{aligned}\frac{d}{dT} \left( \frac{\mu_i^\circ}{T} \right) &= \frac{d}{dT} \left( \frac{\overline{H}_i^\circ - T\overline{S}_i^\circ}{T} \right) = \frac{d}{dT} \left( \frac{\overline{H}_i^\circ}{T} - \overline{S}_i^\circ \right) \\ &= \frac{d}{dT} \left( \frac{\overline{H}_i^\circ}{T} \right) - \frac{d}{dT} (\overline{S}_i^\circ) \\ &= -\frac{\overline{H}_i^\circ}{T^2}\end{aligned}$$

(b) Fun reminders about math:  $\frac{dx}{dy} = \left( \frac{dx}{dz} \right) \left( \frac{dz}{dy} \right)$

Hence, we can express  $\frac{d \ln K}{d(1/T)} = \frac{d \ln K}{dT} \frac{dT}{d(1/T)}$

$$\begin{aligned}\frac{d \ln K}{dT} &= \frac{d}{dT} \left( \frac{-1}{R} \right) \left( \frac{c\mu_c^\circ}{T} + \frac{d\mu_d^\circ}{T} - \frac{a\mu_a^\circ}{T} - \frac{b\mu_b^\circ}{T} \right) \\ &= \left( \frac{-1}{R} \right) \left[ \frac{d}{dT} \left( \frac{c\mu_c^\circ}{T} \right) + \frac{d}{dT} \left( \frac{d\mu_d^\circ}{T} \right) - \frac{d}{dT} \left( \frac{a\mu_a^\circ}{T} \right) - \frac{d}{dT} \left( \frac{b\mu_b^\circ}{T} \right) \right]\end{aligned}$$

Oh boy/girl/it! Now we can use what we proved in part (a). Homework can be so much fun!

$$\begin{aligned}\frac{d \ln K}{dT} &= \left( \frac{-1}{R} \right) \left[ -\frac{c\overline{H}_c^\circ}{T^2} + -\frac{d\overline{H}_d^\circ}{T^2} + \frac{a\overline{H}_a^\circ}{T^2} + \frac{b\overline{H}_b^\circ}{T^2} \right] \\ &= \frac{\Delta H^\circ}{RT^2}\end{aligned}$$

$$\frac{dT}{d(1/T)} : \text{let } x = 1/T \rightarrow \frac{dT}{d(1/T)} = \frac{d}{dx} \left( \frac{1}{x} \right) = -\frac{1}{x^2}$$

now substitute  $1/T$  back in for  $x$

$$\frac{dT}{d(1/T)} = -T^2$$

Chem 130A PROBLEM SET 6 SOLUTIONS, PAGE 2

4.11 continued

$$\frac{d \ln K}{d(1/T)} = \left( \frac{d \ln K}{dT} \right) \left( \frac{dT}{d(1/T)} \right)$$

$$= \left( \frac{\Delta H^\circ}{RT^2} \right) (-T^2) = -\frac{\Delta H^\circ}{R}$$

(14) (a) pH = 9.0 [His]<sub>TOT</sub> = 0.200 M

At a pH of 9.0, the dominant species of histidine will be His<sup>-</sup> and HisH. This is because the pK<sub>a</sub> of the dissociation  $\text{HisH} + \text{H}_2\text{O} \rightleftharpoons \text{His}^- + \text{H}_3\text{O}^+$  is 9.16.\*

We can then assume the following:

$$[\text{His}]_{\text{TOT}} = [\text{His}^-] + [\text{HisH}] = 0.200 \text{ M} \quad \langle \text{eqn. 14-a} \rangle$$

We also know the following:

$$\frac{[\text{H}_3\text{O}^+][\text{His}^-]}{[\text{HisH}][\text{H}_2\text{O}]} = K_a$$

assume this  
is 1 (concentration  
of H<sub>2</sub>O does not change much)

$$\begin{aligned} \text{pH} &= 9.0 \\ -\log [\text{H}^+] &= 9.0 \\ [\text{H}^+] &= 10^{-9.0} \end{aligned}$$

$$\begin{aligned} \text{pK}_a &= 9.16 \\ -\log K_a &= 9.16 \\ K_a &= 10^{-9.16} \end{aligned}$$

\* If you want to see a quick way of verifying this, see the bottom of page 3.

Chem 130A HOME-GROWN PS6 Solutions,  
PAGE 3

4.14 continued:

$$\text{Hence: } \frac{[\text{H}^+][\text{His}^-]}{[\text{HisH}]} = K_a \\ 10^{-9} \frac{[\text{His}^-]}{[\text{HisH}]} = 10^{-9.16}$$

$$[\text{His}^-] = \frac{\downarrow}{10^{-9}} \frac{10^{-9.16} [\text{HisH}]}{10^{-9}}$$

$$[\text{His}^-] = 10^{-0.16} [\text{HisH}]$$

*<eqn. 14-b>*

We can use the above equation along with equation 14-a to solve for  $[\text{His}^-]$  and  $[\text{HisH}]$ .

$$[\text{His}^-] + [\text{HisH}] = 0.200 \text{ M}$$

$$10^{-0.16} [\text{HisH}] + [\text{HisH}] = 0.200 \text{ M}$$

$$[\text{HisH}] = \frac{0.200 \text{ M}}{(1 + 10^{-0.16})} = \frac{0.200}{1.16918} = 0.118 \text{ M}$$

$$[\text{His}^-] = 0.200 \text{ M} - [\text{HisH}]$$

$$= 0.200 \text{ M} - 0.118 \text{ M} = 0.082 \text{ M}$$

\* BOTTOM OF PAGE 3! ~~~~~~  
(in reference to page 2) To find the dominant species in this multi-equilibrium acid dissociation, calculate the ratios of conjugate base to acid using the  $K_a$ 's at  $[\text{H}^+]$ . From the values below the dominance of HisH, His $^-$  is clear

$$\frac{[\text{HisH}_2^+]}{[\text{HisH}_3^{2+}]} = \frac{K_{a_1}}{[\text{H}^+]} = \frac{10^{-1.87}}{10^{-9}} = 10^{7.13}$$

This means that there's much more  $\text{HisH}_2^+$  than  $\text{HisH}_3^{2+}$ .

$$\frac{[\text{HisH}]}{[\text{HisH}_2^+]} = \frac{K_{a_2}}{[\text{H}^+]} = \frac{10^{-6}}{10^{-9}} = 10^3 \quad 1000 \times \text{ more HisH than HisH}_2^+$$

$$\frac{[\text{His}^-]}{[\text{HisH}]} = \frac{K_{a_3}}{[\text{H}^+]} = \frac{10^{-9.16}}{10^{-9}} = 10^{-0.16} \quad \text{slightly less His}^- \text{ than HisH}$$

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4.14 continued

Now, we can also calculate what the concentration of  $\text{HisH}_2^+$  is. We know:



$$\frac{[\text{HisH}][\text{H}^+]}{[\text{HisH}_2^+]} = K_a \quad \text{pH} = 9 \rightarrow [\text{H}^+] = 10^{-9}$$

$$\frac{[\text{HisH}](10^{-9})}{[\text{HisH}_2^+]} = 10^{-6}$$

(remember,  $\text{pH} = 9$ !) we can approximate and use  $[\text{HisH}^+]$  as calculated in the previous part of this problem.

$$\frac{[\text{HisH}](10^{-9})}{[\text{HisH}_2^+]} = 10^{-6} \rightarrow \frac{[\text{HisH}](10^{-9})}{(10^{-6})} = [\text{HisH}_2^+]$$

$$[\text{HisH}_2^+] = \frac{(0.118 \text{ M})(10^{-9})}{(10^{-6})} = 1.18 \times 10^{-4} \text{ M}$$

We can now use  $[\text{HisH}_2^+]$  to calculate  $[\text{HisH}_3^{2+}]$ !

$$[\text{HisH}_3^{2+}] = \frac{[\text{HisH}_2^+][\text{H}^+]}{10^{-1.82}} = \frac{(1.18 \times 10^{-4} \text{ M})(10^{-9})}{10^{-1.82}} = 7.80 \times 10^{-12}$$

$$\frac{\text{H}_2^+}{\text{H}_3^-} = K_a$$

$pK_a$  of initial

dissociation = 1.82

$$\text{To get } [\text{OH}^-]: \frac{K_w}{[\text{H}^+]} = [\text{OH}^-] = \frac{10^{-14}}{10^{-9}} = 10^{-5}$$

To get  $[\text{Na}^+]$  we use charge balance:

$$[\text{Na}^+] + [\text{H}^+] + [\text{HisH}_2^+] + [\text{HisH}_3^{2+}] = [\text{OH}^-] + [\text{His}^-]$$

$$\begin{aligned} [\text{Na}^+] &= [\text{OH}^-] + [\text{His}^-] - [\text{H}^+] - [\text{HisH}_2^+] - [\text{HisH}_3^{2+}] \\ &= 0.082 \text{ M} \end{aligned}$$

4.14 continued

(b) Joy joy joy, let's use the van't Hoff equation.

$$pK_a(25^\circ\text{C}) = 9.16 \quad \text{van't Hoff}$$

$$25^\circ\text{C} = 298\text{ K} = T_1$$

$$40^\circ\text{C} = 313\text{ K} = T_2 \quad \ln \frac{K_2}{K_1} = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Basically, we're doing the same thing we did in part (a), except using a different  $K_a$ , which we calculate via the van't Hoff equation.

$$K_a(25^\circ\text{C}) = K_1 = 10^{-9.16}$$

$$\Delta H^\circ(25^\circ\text{C}) = 43.6\text{ kJ/mol}$$

$$K_2 = ? \quad \text{solve for } K_2$$

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$K_2 = K_1 \exp \left\{ \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right\}$$

$$= (6.92 \times 10^{-10}) \exp \left\{ \frac{-(43.6\text{ kJ/mol})}{8.3145 \times 10^{-3}\text{ kJ/mol K}} \left( \frac{1}{313\text{ K}} - \frac{1}{298\text{ K}} \right) \right\}$$

$$= (6.92 \times 10^{-10})(2.324)$$

$$= 1.608 \times 10^{-9} = K_a(40^\circ\text{C})$$

$$pK_a(40^\circ\text{C}) = 8.79$$

With this new value for  $K_a(40^\circ\text{C})$ , we can calculate  $[\text{H}^+]$  and hence  $\text{pH}(40^\circ\text{C})$ .

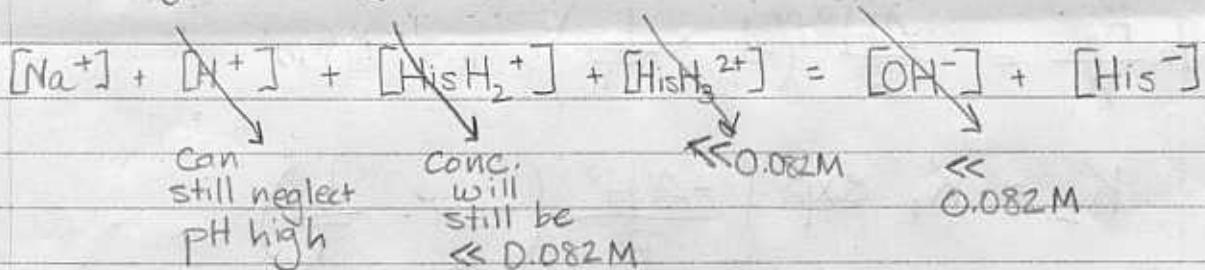
We know that for a  $40^\circ\text{C}$  change, pH will still be high, hence His and HisH are still the main species. Hence

$$[\text{His}]_{\text{total}} \approx [\text{His}] + [\text{HisH}] = 0.2 \text{ M}$$

We also know that  $[\text{Na}^+]$  (from NaOH) should have remained constant:

$$[\text{Na}^+] = [\text{His}^-]_{\text{in part a}} = 0.082 \text{ M}$$

according to charge balance:



$$[\text{Na}^+] \approx [\text{His}^-]$$

$$\therefore [\text{Na}^+] = 0.082 \text{ M}$$

$$[\text{His}^-] = 0.082 \text{ M}$$

$$[\text{HisH}] = 0.200 - [\text{His}^-] = 0.118 \text{ M}$$

$$[\text{H}^+] = \frac{K_a(40^\circ\text{C}) \times [\text{HisH}]}{[\text{His}^-]} = \frac{(1.61 \times 10^{-9} \text{ M})(0.118 \text{ M})}{(0.082 \text{ M})}$$

$$= 2.32 \times 10^{-9} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (2.32 \times 10^{-9}) = \boxed{8.64}$$

414 continued

(c) We just calculated some of the ion concentrations at 40°C. They were:

$$[\text{Na}^+] = 0.082 \text{ M}$$

$$[\text{HisH}] = 0.118 \text{ M}$$

$$[\text{OH}^-] = 10^{-5} \text{ M}$$

$$[\text{H}^+] = 2.32 \times 10^{-9} \text{ M}$$

$$[\text{His}^-] = 0.082 \text{ M}$$

We would like to calculate  $[\text{HisH}_2^+]$  and  $[\text{HisH}_3^{2+}]$ .

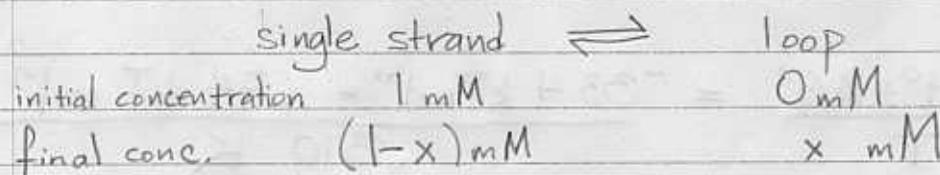
Again, we can use the van't Hoff equation to calculate the new  $K_a$ 's at 40°C.

	$K_a(25^\circ\text{C})$	$K_a(40^\circ\text{C})$	Δ $H^\circ$
$\text{HisH}_3^{2+} \rightleftharpoons \text{HisH}_2^+ + \text{H}^+$	$10^{-1.82}$	$10^{-1.82}$	0
$\text{HisH}_2^+ \rightleftharpoons \text{HisH} + \text{H}^+$	$10^{-6.00}$	$1.78 \times 10^{-6}$	$29.9 \text{ kJ}$

$$[\text{HisH}_2^+] = \frac{[\text{HisH}] [\text{H}^+]}{K_a(40^\circ\text{C})} = \frac{(0.118 \text{ M})(2.32 \times 10^{-9} \text{ M})}{1.78 \times 10^{-6} \text{ M}} = 1.54 \times 10^{-4}$$

$$[\text{HisH}_3^{2+}] = \frac{[\text{HisH}_2^+] [\text{H}^+]}{K_a(40^\circ\text{C})} = \frac{(1.54 \times 10^{-4} \text{ M})(2.32 \times 10^{-9} \text{ M})}{10^{-1.82} \text{ M}} = 2.35 \times 10^{-11}$$

$$(17) (a) T = 25^\circ\text{C} \quad K_1 = 0.86$$



$$K_1 = \frac{[\text{loop}]}{[\text{ss}]} = \frac{x}{(1 \times 10^{-3} \text{ M} - x)} = 0.86$$

$$x = (10^{-3} \text{ M} - x) 0.86$$

$$x = 8.6 \times 10^{-4} \text{ M} - 0.86x$$

$$1.86x = 8.6 \times 10^{-4} \text{ M}$$

$$x = \frac{8.6 \times 10^{-4} \text{ M}}{1.86} = 4.62 \times 10^{-4}$$

$$\rightarrow [\text{loop}] = 4.62 \times 10^{-4} \text{ M}$$

$$\rightarrow [\text{ss}] = 10^{-3} - x$$

$$= 5.38 \times 10^{-4} \text{ M}$$

YOU KNOW THEY'RE GOOD FOR YOU!!!

4.17 continued

Increasing  $[ss]$  should not have any effect upon the FRACTION of the hairpin loop, because the ratio of  $[ss]$  to  $[loop]$  must remain constant to maintain  $K_1 = 0.86$ . If the solution were non-ideal, the actual numerical fraction could vary.

$$(b) T = 37^\circ\text{C} \rightarrow (37 + 273)\text{K} = 310\text{ K}$$

$$K = 0.51$$

$$\Delta G^\circ = -RT \ln K = -(8.3145 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1})(310\text{K}) \ln(0.51)$$

$$= 1.74 \text{ kJ mol}^{-1}$$

use van't Hoff eqn for  $\Delta H$ :

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\frac{-R \ln(K_2/K_1)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \Delta H^\circ = \frac{-(8.3145 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1}) \ln(0.51/0.86)}{\left(\frac{1}{310} - \frac{1}{298}\right)}$$

$$= -33.4 \text{ kJ/mol}$$

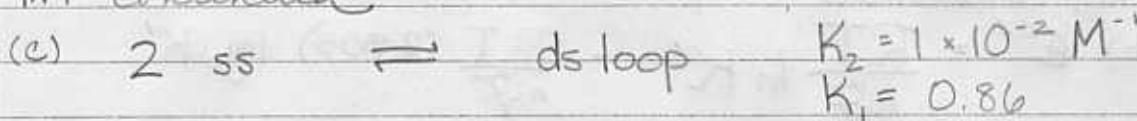
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

↓

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-33.4 \text{ kJ mol}^{-1} - 1.74 \text{ kJ mol}^{-1}}{310 \text{ K}} \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right)$$

$$= -113 \text{ J mol}^{-1} \text{ K}^{-1}$$

4.17 continued



$$[\text{ss}]_0 = 0.100 \text{ M}$$

We know that after equilibrium is reached:

$$[\text{ss}]_0 = 0.100 \text{ M} = [\text{ss}] + [\text{loop}] + 2[\text{dsloop}]$$

We also know:

$$K_2 = \frac{[\text{dsloop}]}{[\text{ss}]^2} \quad K_1 = \frac{[\text{loop}]}{[\text{ss}]}$$

Here we have three equations with three unknowns.  
That means we can solve for all three variables.

$$K_1[\text{ss}] = [\text{loop}] \quad K_2[\text{ss}]^2 = [\text{dsloop}]$$

$$0.100 \text{ M} = [\text{ss}] + K_1[\text{ss}] + 2K_2[\text{ss}]^2$$

rearrange this a bit:

$$2K_2[\text{ss}]^2 + (1 + K_1)[\text{ss}] - 0.100 \text{ M} = 0$$

$$2 \times 10^{-2} \text{ M}^{-1} [\text{ss}]^2 + (1.86)[\text{ss}] - 0.100 \text{ M} = 0$$

$$\text{solve quadratic equation: } [\text{ss}] = 0.0537 \text{ M}$$

plug  $[\text{ss}]$  into other two equations:

$$[\text{dsloop}] = K_2[\text{ss}]^2 = 1 \times 10^{-2} \text{ M}^{-1} (0.0537 \text{ M})^2 = 2.88 \times 10^{-5} \text{ M}$$

$$[\text{loop}] = K_1[\text{ss}] = (0.86)(0.0537 \text{ M}) = 0.0462 \text{ M}$$

(21) (a) Calculation of  $K'$ . The tic mark means we are using the biochemist's standard state. At  $\text{pH} = 7$ ,  $a_{\text{H}^+} = 1$ .

$$K' = \frac{a_{\text{H}^+} a_{\text{Fd}_{\text{red}}}}{a_{\text{H}_2}^{1/2} a_{\text{Fd}_{\text{ox}}}}$$

$$= \frac{(1) \left(\frac{1}{3} (\text{total Fd})\right)}{(1) \left(\frac{2}{3} (\text{total Fd})\right)} = \frac{1}{2} = \underline{\underline{0.5}}$$

$a_{\text{H}_2} = 1$  because  $P_{\text{H}_2} = 1 \text{ atm}$ .  
(We assume ideal gas behavior.)

The answer key in the back of your book says  $(5 \times 10^{-8})$  but that is DOOFUS because that's where  $a_{\text{H}^+} = 10^{-7}$  the chemist's std. state

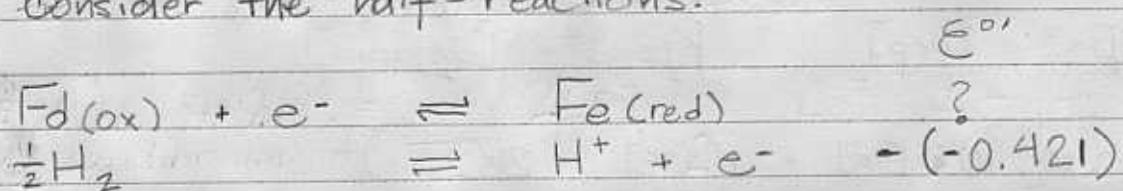
4.21, continued

$$(b) \text{whole rxn } E^{\circ'} = \frac{RT}{nF} \ln K' - \frac{RT}{nF} (2.303) \log_{10} K'$$

$$= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) (2.303) \log_{10} 0.5}{(96,485 \text{ C mol}^{-1})}$$

$$= -0.0178 \text{ JC}^{-1} = -0.0178 \text{ V}$$

As you see, we've only calculated  $E^{\circ'}$  for the whole reaction. To obtain  $E^{\circ'}(\text{Fd(red)/Fd(ox)})$ , we need to consider the half-reactions:



Note that the value of  $E^{\circ'}$  does NOT change with respect to the actual stoichiometric coefficients in the half-reactions.

$$E^{\circ'}_{\text{total}} = E^{\circ'}_{\text{Fd}} - E^{\circ'}_{\text{H}^+/\text{H}_2} \leftarrow \text{we can obtain this easily by thinking about this whole redox reaction as a galvanic cell;}$$

$$E^{\circ'}_{\text{total}} + E^{\circ'}_{\text{H}^+/\text{H}_2} = E^{\circ'}_{\text{Fd}}$$

$$-0.0178 \text{ V} - 0.421 \text{ V} = E^{\circ'}_{\text{Fd}}$$

$$= -0.439 \text{ V}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Some memory devices for electrochemistry:

O I L      R I G  
 Oxidation means Loss of Electrons  
 Reduction means Gain of Electrons

OLE

Oxidation means Loss of Electrons

Cats like to chase and catch things, therefore the cathode is where electrons are caught and eaten up!

③  $c = [S]_0$  = initial concentration of single strands  
 $f$  = fraction of single strands that are double strands @ equilibrium

$$\text{# double strands} = \frac{fc}{2} = [D] \quad [S] = c - fc \\ @ \text{equilibrium} \quad \quad \quad = c(1-f)$$

$$K = \frac{[D]}{[S]^2} = \frac{fc}{2c(1-f)^2} = \frac{f}{2c(1-f)^2}$$